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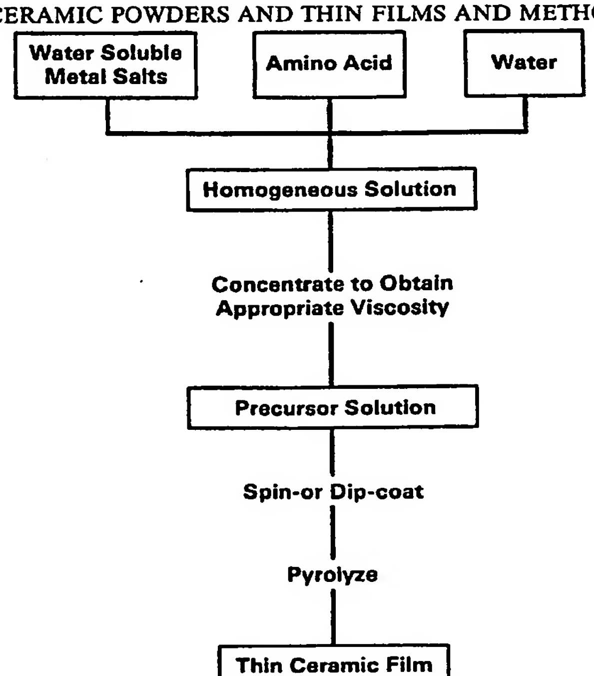

(57) Abstract

This invention is directed to the formation of homogeneous, aqueos precursor mixtures of at least one soluble metal salt and amino acid. This produces, upon evaporation, a substantially homogeneous intermediate material having a concentration which would support combustion. A metal oxide powder results on ignition of the intermediate product which combusts same to produce the product powder. An aqueous solution of metal nitrates or other soluble metal salts and a low molecular weight amino acid is coated onto a substrate and pyrolyzed to form a thin ceramic film. The amino acid serves to prevent precipitation of individual solution components, forming a very viscous liquid as excess water is evaporated.

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METAL OXIDE CERAMIC POWDERS AND THIN FILMS AND METHODS OF MAKING SAME

BACKGROUND OF THE INVENTION

This invention relates to metal oxide powders and thin films useful in the production of various ceramic materials, and to processes for making such metal oxide ceramic powders, particularly metal oxide ceramic powders of fine particle size and such thin ceramic films.

Fine particle size (0.1-1.0 micron diameter), metal oxide powders are highly desirable in ceramic product manufacturing. Sintering of these fine powders occurs at temperatures much lower than most larger-sized commercial powders.

The traditional methods for producing ceramic powders involve mechanically mixing the component oxides in their appropriate stoichiometric amounts, calcining the solution at high temperature to obtain a single phase, and mechanically milling the product to obtain the desired particle size. However, high temperature calcination promotes crystal growth, which is an undesirable effect, the desired end product being a fine-grained ceramic powder. On the other hand, mechanical milling often introduces unwanted impurities into the final ceramic powder product.

A number of somewhat complicated chemical methods have been developed to produce fine ceramic powders. Included are controlled hydrolysis and condensation of metal alkoxides (sol gel), flame oxidation, and spray drying of a colloidal suspension, freeze-drying, and coprecipitation.

In U.S. Patent 3,330,697, a method of producing electrical capacitors is described employing lead and alkaline earth titanates, zirconates and niobates. These compounds are used in selected combinations and proportions to form resin intermediates. Calcination

of the resin intermediates removes the organic material and leaves a metal oxide powder, ideally in a finely divided state. A list of compounds which can be used in this process are provided in column 2, lines 62-67.

In a subsequent article in Mat. Res. Soc. Symp. Proc., Vol. 32, pages 239-244 (1984), entitled, Preparation Of Strontium Titanate Ceramics In Internal Boundary Layer Capacitors By The Pechini Method, by Budd, et al., strontium titanate is described as one of the titanate perovskite materials that are widely used in the electronic ceramics industry. In the study described in the article, a liquid resin-forming technique, as described in the above U.S. 3,330,697 patent was used to prepare the strontium titanate powders.

In an article entitled, Preparation of Fine Organic Powders by Evaporative Decomposition Solutions, by D.M. Roy, et al., in Am. Ceram. Soc. Bull., Vol 56, at page 1023 (1977), the authors describe ceramic powder production by evaporative decomposition of solutions. Specifically, aluminum oxide and calcium aluminum oxide powders were prepared in laboratory scale furnaces using the EDS technique. Details of the furnace and atomizer assembly, respectively, employed in the EDS method are set forth in FIGS. 1 and 2 of the Roy article.

A wide variety of thin ceramic films have also been prepared by various vacuum techniques and by chemical methods. These methods are described in the following references:

1. H. Schroeder, Phys. Thin Films, 5, 87 (1969).
2. B.E. Yoldas and T.W. O'Keefe, Appl. Opt., 18, 3133 (1979).
3. C. Feldman, J. appl. Phys. 27, 870 (1956)
4. M.G. Pechini, United States Patent 3,330,697 (1967).

A relatively large volume of other articles have been written concerning various chemical routes to production of thin ceramic films. Two books, Better Ceramics Through Chemistry, eds. C.J. Brinker, D.E. Clark, and D.R. Ulrich, Materials Research Society Proceedings, Volume 32, North-Holland, New York, 1984, and Better Ceramics Through Chemistry II, eds. C.J. Brinker, D.E. Clark, and D.R. Ulrich, Materials Research Society Symposia Proceedings, Volume 73, Materials Research Society, Pittsburgh, PA 1986, contain a number of pertinent articles. Vacuum techniques generally suffer from the requirement of relatively sophisticated apparatus and/or area and geometrical constraints. Advantages of chemical solution methods include simplicity, low cost, and precise control of film stoichiometry.

Accordingly, a need exists for a process for producing ceramic powders, particularly fine, single-phase ceramic powder, without the use of complex equipment such as the above-described EDS furnace, which can be produced in a direct manner with a minimum amount of skill and labor, and which provides a high-quality product. A need also exists for a very simple method to prepare thin ceramic films, particularly thin ceramic films from an aqueous solution of metal nitrates and an amino acid.

SUMMARY OF THE INVENTION

This invention is directed to metal oxide powders, and to methods for making same, and overcomes some of the above problems associated with the prior art processes for producing ceramic powders. The process of this invention is direct and relatively simple, requiring a minimum level of skill and labor to complete, is relatively low cost, and produces a fine

metal oxide powder which is high in quality and which is typically formed as a single-phase ceramic powder.

The process generally includes the formation of homogeneous, aqueous precursor mixtures of at least one substantially soluble metal salt and a substantially soluble, combustible co-reactant compound, typically an amino acid. This produces, upon evaporation, a substantially homogeneous intermediate material having a concentration which would support combustion. The homogeneous intermediate material essentially comprises highly dispersed or solvated metal constituents and the co-reactant compound. The intermediate material is quite flammable. A metal oxide powder results on ignition of the intermediate product, which combusts same to produce the product powder. The combustion step is typically conducted at a temperature which will consume substantially all of the amino acid compound, but which will neither substantially melt the metal oxide powder nor cause the loss of volatile components thereof. Combustion should therefore be conducted to avoid a substantial loss of stoichiometry or the formation of incorrect crystalline phases in the metallic oxide powder product. Calcination of the product can then be conducted to remove any residual organic phase so that submicron ceramic particles of the above-described metal oxide powder are obtained.

It also provides a new route to producing thin ceramic films from an aqueous solution of metal nitrates and a low molecular weight amino acid. Films can be prepared at room temperature by spraying or by spin- or dip-coating a substrate of choice with the metal nitrate/amino acid solution, followed by pyrolysis. The amino acid serves to prevent precipitation of individual solution components, forming a very viscous liquid as excess water is evaporated. Breakdown products of the amino acid and

nitrate ions are removed from the thin film during pyrolysis. Employing inexpensive and readily available materials, the method appears applicable to the production of a wide range of thin ceramic film compositions. Depending on their compositions, these films have utility as superconductors, in sensors, as anti-corrosion coatings, as abrasion-resistant coatings, as optical coatings, or for other uses.

The foregoing and other objects, features and advantages of the invention will become more readily apparent from the following detailed description of a preferred embodiment which proceeds with reference to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart outlining the steps of producing thin ceramic films.

FIG. 2 is a graph showing a thermogravimetric analysis of the metal nitrate/glycine/aqueous solution used to produce thin films of the high critical temperature superconductor, $YBa_2Cu_3O_{7-x}$. Decomposition of the organic components and the nitrates was complete by approximately 700°C.

FIG. 3 is a secondary ion mass spectrometry (SIMS) depth profile of a yttria-stabilized zirconia layer (20 mole % Y_2O_3) on Al_2O_3. The depth scale was determined using a stylus profilometer. Because of differing sensitivities of the SIMS technique to the various components, the signal intensities should not be taken as an absolute reflection of composition, but rather an indication of the variation in composition of an individual component as a function of depth.

FIG. 4 is a SIMS depth profile of a spin-coated $YBa_2Cu_3O_{7-x}$ film on SiO_2 that had been precoated with a yttria-stabilized zirconia barrier layer. The purpose

of the buffer layer was to prevent interactions between the superconducting film and the substrate.

DETAILED DESCRIPTION OF THE INVENTION

Metal Oxide Ceramic Powers

This invention comprises the production of metal oxide ceramic powders from an initial precursor aqueous solution of a corresponding metal salt and an amino acid. The particular metal elements of the metal salts that can be used in the process of this invention are those which will form a substantially water soluble salt and can be converted to a metal oxide during burning of the metal salt/amino acid/water solution. This is contrary to the U.S. 3,330,697 patent which states that compounds such as nitrates did not serve the objectives of that invention. Metal cations that are useful in producing the metal oxide powders of this invention are aluminum, calcium, chromium, manganese, iron, nickel, copper, strontium, yttrium, zirconium, silver, thallium, barium, lanthanum and bismuth, as well as lithium, sodium, magnesium, potassium, scandium, zinc, rubidium, cadmium, indium, cesium, mercury, lead, cerium, praseodymium, nedymium, samarium, europium, gadolianium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, uranium, thorium, cobalt, zinc, hafnium and molybdenum respectively.

The anions which are particularly useful in this invention are those which exhibit substantial solubility in aqueous mixture, and which decompose with little or no residue during ignition of the metal salt/amino acid aqueous precursor mixture. Anions suitable for use in this process include acetates, formates, halides (particularly chlorides, bromides, iodides), oxyhalides (particularly perchlorates, perbromates, periodates, chlorates, bromates, iodates,

chlorites, bromites, and iodites), sulphates, carbonates and nitrates, respectively. However, the anion of choice is the nitrate ion. Nitrate compounds are quite soluble in water, are widely available, and are stable in a water mixture. Nitrates also provide oxygen to combust the amino acids. Very little residue (less than 1%) remains in the ash after ignition of a metal nitrate/amino acid mixture. Furthermore, any residue from the use of nitrates can be essentially eliminated by calcining the ash at a temperature of about 600-700°C.

Metal salt reactants capable of producing the powders of the present invention include the following compounds: Lanthanum nitrate hydrate, such as $La(NO_3)_3 \cdot 6H_2O$; strontium nitrate, anhydrous; chromium nitrate hydrate, such as $Cr(NO_3)_3 \cdot 9H_2O$; yttrium nitrate hydrate, such as $Y(NO_3)_3 \cdot 6H_2O$; calcium nitrate hydrate, such as $Ca(NO_3)_2 \cdot 4H_2O$; barium nitrate; copper nitrate hydrate, such as $Cu(NO_3)_2 \cdot 3H_2O$; bismuth nitrate hydrate, such as $Bi(NO_3)_3 \cdot 5H_2O$; nickel nitrate hydrate, such as $Ni(NO_3)_2 \cdot 6H_2O$; iron nitrate hydrate, such as $Fe(NO_3)_2 \cdot 6H_2O$; zirconium nitrate pentahydrate, manganese (II) nitrate tetrahydrate, aluminum nitrate hydrate, such as $Al(NO_3)_3 \cdot 9H_2O$, cerium nitrate hydrate such as $Ce(NO_3)_4 \cdot 6H_2O$ or combinations of these metal salt reactants.

The co-reactant, particularly an amino acid, is combined with a metal salt in aqueous mixture to produce the subject precursor material. It is important that the co-reactant compound employed have a relatively high water solubility, good complexing properties, and, after evaporation, will combust with as little residue as possible. The amino acid of choice is glycine because it the simplest amino acid, is readily available, inexpensive, and requires the least amount of oxidant to combust. Other amino acids

such as glycine, alanine, valine, leucine, isoleucine, proline, aspartic acid, glutamic acid, lysine, arginine, histidine, asparagine, glutamine, serine, threonine, phenylalanine, tyrosine, and tryptophan can be suitable in this invention.

In the precursor mixture, the ratio of amino acid to metal cation is from about a mole ratio of 0.5:1 up to a ratio of about 6:1. The best product usually results when the glycine-to-cation molar ratio is adjusted to produce the largest bulk volume of ash. Sufficient water is added to dissolve the metal salts and the amino acid.

Ammonium nitrate and additional amino acid may be added to the aqueous solution of metal nitrates and amino acid to increase the bulk volume of the ash produced.

The precursor mixture may be formed in some instances under acidic or basic conditions. However, it is preferred that the pH of the mixture be approximately neutral.

The precursor mixture is formed into an intermediate material, preferably in the form of a glass-like intermediate material, by evaporating water therefrom. The amine and carboxylic acid end groups of the amino acid bind with the metal cations in mixture, thereby increasing the solubility of the metal salt and inhibiting inhomogeneous precipitation thereof. Thus, as the precursor aqueous mixture is concentrated by evaporation of excess water, a material results, in which diffusion and therefore precipitation of individual components, is inhibited.

The intermediate material has a relatively low ignition temperature, and can be easily heated to the point of autoignition. For example, the autoignition temperature of an intermediate formed from lanthanum

nitrate hydrate, strontium nitrate, and chromium nitrate hydrate is about 200°C.

When the precursor solution is ignited, the nitrate or other anion usually serves as the principal oxidizer for the combustion of the amino acid. Oxygen from the air may also participate in combustion of some of the amino acid, depending on the ratio of amino acid to nitrate in the precursor solution and the identity of the amino acid. However, the combustion temperature and the general vigor of the combustion reaction decreases as the required amount of air increases. For example, in the case of $(La,Sr)CrO_3$ prepared from the metal nitrates and glycine, the most vigorous combustion and highest combustion temperatures occurred when two glycine molecules were present in the precursor solution for every three nitrate ions, which corresponds to about two glycine molecules per metal cation. When the quantity of glycine was increased to one glycine molecule per nitrate ion, or three glycine molecules per metal cation, the combustion reaction was much slower and occurred at a much lower temperature.

Thus, combustion generally occurs at a temperature that will consume substantially all of the amino acid, but will neither substantially melt the metal oxide powder (which causes excessive sintering of the particles), nor volatilize any of the metal oxide components causing substantial loss of stoichiometry of the final powder product. Control over the combustion temperature therefore can be very important. Excessive sintering of the ceramic powder particles will result if the combustion temperature is at too high a level so that the particles melt; loss of some of the more volatile components can also occur at the highest combustion temperatures. For example, for the high critical temperature superconductor yttrium barium cuprate, use of three glycine molecules for every four

nitrate ions, equivalent to two glycine molecules per metal cation, gave a combustion temperature that was too high to form a useful powder. The ceramic particles sintered to form large, porous chunks; the product also was not superconducting after the usual thermal processing, indicating some loss of stoichiometry or formation of incorrect crystalline phases. However, when nine glycine molecules were present for every eight nitrate ions, equivalent to three glycine molecules per metal cation, particles formed were submicron in diameter; with subsequent thermal processing, the product exhibited superconducting properties. Refractory ceramic materials such as $(La,Sr)CrO_3$, because of their much higher melting temperatures, are much less sensitive to the combustion temperature. Acceptable products can be formed over a much wider range of amino acid to metal or nitrate ratios in the precursor solution.

Although very little residue remains in the ash after ignition of the metal salt/amino acid intermediate material, any remaining nitrate or carbon can be driven off and essentially eliminated by volatizing same by calcination or other like techniques. Typically, calcination can be accomplished at temperatures of 700°C, or less, using readily available equipment, such as a common laboratory muffle furnace or the like. The metal oxide particles will generally grow in size during the calcination process.

Metal oxide powder products which can be produced by this invention include the following: lanthanum strontium chromite, yttrium calcium chromite, lanthanum strontium manganite, yttrium calcium manganite, yttrium barium copper oxide, bismuth calcium strontium copper oxide, nickel oxide-nickel ferrite, yttria-stabilized zirconia, calcium zirconate, strontium zirconate, manganese ferrite, lanthanum strontium ferrite,

zirconium aluminate, cerium zirconium oxide and lanthanum strontium aluminum chromite. The structure formulae of specific metal oxide materials which can be produced by this invention are as follows: $La_{1-x}Sr_xCrO_3$, where x = 0 to 1.0; $Y_{1-x}Ca_xCrO_3$, where x = 0 to 1.0; $YBa_2Cu_3O_{7-x}$, where x = 0.06; $Bi_2CaSr_2Cu_2O_9$; NiO-$NiFe_2O_4$; 0-20% mole percent Y_2O_3,ZrO_2; $CaZrO_3$; $SrZrO_3$; $MnFe_2O_4$; $La_{0.75}Sr_{0.25}FeO_3$; $(ZrO_2)_x(Al_2O_3)_{1-x}$, where x = 0.0 to 1.0; $La_{1-x}Sr_xMnO_3$, where x = 0.0 to 1.0; $Y_{1-x}Ca_xMnO_3$, where x = 0.0 to 1.0; $CeO_2 \cdot ZrO_2$, and $La_{1-y}Sr_yCr_{1-x}Al_xO_3$, where y = 0 to 0.3 or x = 0 to 0.3.

The fine, metal oxide particles of this invention are useful in numerous ceramic applications. Primary metal oxide particles are typically in a narrow particle size distribution range, and are generally not more than about 1 micrometer (1000 nm) in diameter. More specifically, the fine particles produced by the process of the present invention are of a submicron particle size, the primary particle diameter being preferably in the range of about 10 to 700 nm, and more preferably about 20 to 500 nm, and most preferably about 20 to 300 nm.

The subject metal oxide powders can comprise a single crystalline phase, if such is desired, as determined by X-ray diffraction (XRD) analysis. For example, X-ray diffraction analyses were performed for the calcined (750°C for 4 hrs) and uncalcined ash of the composition $La_{0.84}Sr_{0.16}CrO_3$. The uncalcined ash of that composition gave only diffraction lines expected for materials which have a perovskite structure, but were broadened due to the very small particle size of the product. More importantly, no diffraction lines were visible corresponding to individual reactant component oxides or phases other than $La(Sr)CrO_3$ which indicated that the metal oxide powders were single-phased.

The submicron particles of the invention herein have a relatively high surface area, particularly in view of their submicron size. For example, particles of the composition $La_{0.84}Sr_{0.16}CrO_3$ exhibit a BET surface area of about 25 square-meters per gram.

EXAMPLE 1

Lanthanum strontium chromite fine ceramic powders were produced according to the present invention. This material can be used as bipolar or current interconnecting material in the previously described solid oxide fuel cells. Lanthanum strontium chromite is very difficult to produce by conventional methods.

The following describes a preferred preparation method of $La_{1-x}Sr_xCrO_3$:

0.0084 moles of lanthanum nitrate hydrate [$La(NO_3)_3 \cdot 6H_2O$], 0.0016 moles of strontium nitrate, anhydrous [$Sr(NO_3)_2$], 0.01 moles of chromium nitrate hydrate [$Cr(NO_3)_3 \cdot 9H_2O$], 0.06 moles of glycine [$HOOC-CH_2-NH_2$], appropriate to prepare 0.01 moles of $La_{0.84}Sr_{0.16}CrO_3$, were dissolved in a minimum quantity of deionized water. The three metal nitrates and glycine formed a homogeneous, aqueous precursor mixture. The precursor mixture was heated on a hot plate (or in an oven) to evaporate a substantial portion of the water, until the concentration of the solution was approximately 1 mole/liter in terms of the product oxide phase.

Approximately 15 ml (at a time) of the concentrated solution was placed in a 1,000 ml glass beaker. This small aliquot was heated on a hot plate until it boiled, evaporating the remaining free water. The viscous, evaporated precursor solution was then further heated until the autoignition temperature was reached.

The mixture temperature was raised to approximately 200°C and autoignition of the evaporated precursor mixture occurred. The residual ash left in the beaker after autoignition consisted of low density ash containing very fine primary particles of (La,Sr)CrO_3. The residual ash was calcined at approximately 650°C for 4 hours to drive off volatile residuals, which constituted less than one weight percent of the ash.

Fine primary ceramic particles were formed having diameters ranging between approximately 20 and 100 nanometers, and consisting of one crystalline phase. These submicron powders had a surface area greater than 20 square meters per gram. These particles were sinterable in air at 1550°C to a density of greater than 95 percent of their theoretical density.

X-ray diffraction analyses were performed for the uncalcined ash and for ash calcined at 650°C for 4 hours. The uncalcined ash gave only diffraction lines expected for the perovskite structure, but were somewhat broadened due to the very small particle size of the powder. Most importantly, no diffraction lines were visible corresponding to the individual component oxides (Cr_2O_3, SrO, or La_2O_3) of the ceramic oxide product or phases other than (La,Sr)CrO_3. Following calcination, diffraction lines sharpened, due to growth of ceramic particles within the ash. 0.01 moles (approximately 2.3 grams) of $La_{0.84}Sr_{0.16}CrO_3$ powder were produced by the process of this invention.

EXAMPLE 2

The procedure outlined in Example 1 was repeated with the exception of the use of different starting materials, as follows:

yttrium nitrate hydrate [$Y(NO_3)_3 \cdot 6H_2O$]
calcium nitrate hydrate [$Ca(NO_3)_2 \cdot 4H_2O$]

chromium nitrate hydrate [$Cr(NO_3)_3 \cdot 9H_2O$]

Yttrium calcium chromite compounds are closely related to the $(La,Sr)CrO_3$ compounds in Example 1. Both families of compounds are known to be stable at high temperature and to exhibit good electrical properties. Submicron, single-phase $(Y,Ca)CrO_3$ powders were prepared of the structural formula $Y_{(1-x)}Ca_xCrO_3$.

EXAMPLE 3

0.01 moles (approximately 6.6 grams) of the high temperature oxide ceramic material $YBa_2Cu_3O_{7-x}$, where superconducting properties are optimized for x=0.06, was prepared. High temperature superconductors are likely to find wide application in energy conservation technology, sensors, magnets, and magnetic shielding. The procedure of Example 1 was repeated using the following starting materials in their appropriate stoichiometric quantities:

0.01 moles of yttrium nitrate hydrate [$Y(NO_3)_3 \cdot 6H_2O$]

0.02 moles of barium nitrate

0.03 moles of copper nitrate hydrate [$Cu(NO_3)_2 \cdot 3H_2O$]

The product $YBa_2Cu_3O_{7-x}$ ceramic powder was pressed into a pellet and sintered to the orthorhombic phase at approximately 950°C. The pellets were furnace cooled to 450°C and annealed in flowing oxygen at that temperature. The critical temperature for pellets made using this method is greater than 88°K.

EXAMPLE 4

Preparation of a $Bi_2CaSr_2Cu_2O_9$ powder followed the procedure outlined in Example 1, except for the use of the following starting materials.

calcium nitrate hydrate [$Ca(NO_3)_2 \cdot 4H_2O$]

bismuth nitrate hydrate [$Bi(NO_3)_3 \cdot 5H_2O$]

copper nitrate hydrate [$Cu(NO_3)_2.3H_2O$]

strontium nitrate [$Sr(NO_3)_2$]

This composition has also been shown to exhibit superconducting properties above the temperature of liquid nitrogen.

EXAMPLE 5

Nickel oxide-nickel ferrite powders were prepared using the procedure of Example 1, except for the following starting materials:

nickel nitrate hydrate [$Ni(NO_3)_2.6H_2O$]

iron nitrate hydrate [$Fe(NO_3)_2.6H_2O$]

The mixed phase ceramic nickel oxide-nickel ferrite [$NiO-NiFe_2O_4$] may be used as an inert anode in the refining of aluminum metal. The material is known to have good electronic conductivity and has good corrosion resistance in the extreme environments of aluminum refining.

EXAMPLE 6

Zirconia and yttria-stabilized zirconia (0-20 mole percent Y_2O_3) were prepared using the procedure of Example 1, except that the starting materials are zirconium nitrate pentahydrate, yttrium nitrate hexahydrate, and glycine.

The ceramic product material is known to be stable at elevated temperatures, and has found use in sensor technology, wear-resistant materials, and corrosion-resistant materials, among numerous other uses.

EXAMPLE 7

Using the same procedure as described in Example 1, calcium nitrate tetrahydrate and zirconium nitrate pentahydrate were combined to produce a calcium zirconate ceramic powder. Calcium zirconate is a refractory material having good electrical properties.

EXAMPLE 8

Using the same procedure as described in Example 1, strontium nitrate and zirconium nitrate pentahydrate were combined to produce strontium zirconate. Strontium zirconate is a refractory material with good electrical properties.

EXAMPLE 9

Using the same procedure as described in Example 1, manganese (II) nitrate tetrahydrate and iron (II) nitrate hexahydrate were combined to produce manganese ferrite. Manganese ferrite is a refractory ceramic with good magnetic and electronic properties.

EXAMPLE 10

Using the same procedure as described in Example 1, lanthanum nitrate hexahydrate, strontium nitrate, and iron (II) nitrate hexahydrate were combined to produce lanthanum strontium ferrite. Lanthanum strontium ferrite is a refractory ceramic with good magnetic and electronic properties.

EXAMPLE 11

Using the same procedure described in Example 1, lanthanum nitrate hexahydrate, strontium nitrate, and manganese (II) nitrate tetrahydrate were combined to produce lanthanum strontium manganite, of the formula $La_{1-x}Sr_xMnO_3$, where x = 0.0 to 1.0. Lanthanum strontium anganite is a refractory ceramic with good magnetic and electrical properties.

EXAMPLE 12

Using the same procedure described in Example 1, yttrium nitrate hexahydrate, calcium nitrate tetrahydrate, and manganese (II) nitrate tetrahydrate

were combined to produce yttrium calcium manganite, of the formula $Y_{1-x}Ca_xMnO_3$, where x = 0.0 to 1.0. Yttrium calcium manganite is a refractory ceramic with good magnetic and electrical properties.

EXAMPLE 13

Using the same procedure described in Example 1, zirconium nitrate pentahydrate and aluminum nitrate nonahydrate were combined to produce an aluminum oxide-zirconium oxide composite. This material has applications as a structural ceramic.

EXAMPLE 14

Using the same procedure described in Example 1, cerium nitrate hexahydrate and zirconium nitrate pentahydrate were combined to produce ceria-zirconia $CeO_2 \cdot ZrO_2$). This refractory ceramic has good electrical properties.

EXAMPLE 15

Using the same procedure as described in Example 1, lanthanum nitrate hydrate, strontium nitrate, aluminum nitrate hydrate, and chromium nitrate hydrate were combined to produce lanthanum strontium aluminum chromite $La_{1-y}Sr_yCr_{1-x}Al_xO_3$, where y = 0.0 to 0.3 and x = 0.0 to 0.3. This refractory ceramic exhibits good electrical conductivity.

Film Formation

This invention also comprises the production of metal oxide ceramic thin films.

An aqueous precursor solution is prepared containing the nitrate salts of the metal and a low molecular weight amino acid, such as glycine. Metal cation concentrations will normally be in the range of 10^{-3} to 1 molar, with a typical value of 0.5 molar,

whereas the amino acid/metal cation ratio will normally be in the range of 1 to 6, with a typical value of 3. The solution may be concentrated by evaporation, with the purpose of adjusting the viscosity of the solution to facilitate coating steps. A flow chart showing the process is given in Fig. 1.

Film deposition onto a given substrate is accomplished by spin- or dip-coating, followed by pyrolysis at temperatures appropriate for the specific ceramic system. For spin-coatings, typical rotation rates are 1000-3000 rpm.

Pyrolysis of metal nitrate/amino acid thin films are usually performed in air at 700°C or higher temperatures. The thermogravimetric data of Fig. 2 show pyrolysis to be essentially complete at 700°C at a heating rate of 5°C per minute. Typical thickeners of the pyrolyzed films are 100 to 300 nm, although quality films of either greater or lesser thickness may be produces by this method. Depending on the specific ceramic system being considered, further heating to higher temperatures may be required to obtain the desired crystalline phase. For example, thin films of the high T_c superconductor $YBa_2Cu_3O_{7-x}$ required heating at 950°C for 1 to 5 minutes to obtain the tetragonal phase, followed by slow-cooling to 650_oC to transform the layer to obtain the desired orthorhombic phase.

Film Characterization

Thermogravimetric analysis (TGA) was used to reveal the various stages of decomposition of the precursor solution to a final ceramic film. Quadruple mass spectrometry was used to identify gases released during pyrolysis. Film thicknesses were obtained from interference fringes using an ultraviolet-visible spectrophotometer. Compositional depth profiles of the pyrolyzed thin films were obtained using SIMS. Stylus

profilometer measurements were used to establish a relation between actual dept and sputtering time in the SIMS analyses. X-ray photoelectron spectroscopy (XPS) was used to assess the quantity of impurities incorporated within the thin films.

Results and Discussion

Complexation and viscous liquid properties of the low molecular weight amino acid are essential to this invention. The amine and carboxylic acid end groups securely bind metal cations in the aqueous solution, thereby both enhancing the solubility and inhibiting inhomogenous precipitation. The metal nitrate/amino acid/water solutions are concentrated to optimize the solution viscosity for spin- or dip-coating. As the precursor solution is concentrated through evaporation of excess water, a viscous liquid results, which is free of precipitates.

As given in Fig.2, decomposition of the thin film precursor (composed of metal nitrates, an amino acid, and water) occurred in several stages. Water and glycine volatilization was essentially complete by 300^{o}C; nitrate decomposition occurred in several stages and was complete at 700^{o}C when heated at a rate of 5^{o}C/h. Mass spectroscopic analysis of the off-gases revealed that a significant fraction of the amino acid was oxidized by nitrate ions to water, carbon monoxide, carbon dioxide, and nitrogen monoxide; however, some molecular glycine was also detected. Other than a small quantity of residual carbon, XPS analysis detected no contaminants within the pyrolyzed thin films.

To date, the method described here has been demonstrated for the high critical temperature superconductor $YBa_2Cu_3O_{7-x}$, for several compositions in the series (La,Sr)CrO_3, and for several zirconia

compositions including unstabilized, partially stabilized (9 mole % Y_2O_3), and fully stabilized (20 mole % Y_2O_3) zirconia. A SIMS depth profile of a fully stabilized zirconia film on alumina is given in Fig. 3. The lack of detection of aluminum above the noise level in the SIMS profile at the outer surface is an indication of the excellent uniformity of this film. In Fig. 4, a SIMS depth profile of a $YBa_2Cu_3O_{7-x}$ superconducting film deposited on a yttria-stabilized zirconia buffer layer on alumina is given. Thus, it is clear that multiple layers having quite complex compositions can be deposited onto a substrate using this method. It is expected that this new chemical route can be applied to a much wider variety of thin ceramic fils than are described here.

Having illustrated and described the principles of my invention in a preferred embodiment thereof, it should be readily apparent to those skilled in the art that the invention can be modified in arrangement and detail without departing from such principles. I claim all modifications coming within the spirit and scope of the accompanying claims.

We claim:

1. A process for producing a metal oxide powder, which comprises

forming a substantially homogeneous, aqueous precursor mixture comprising at least one substantially soluble metal salt and a substantially soluble, combustible amino acid compound;

evaporating said precursor mixture to form a substantially homogeneous intermediate material having a concentration which will support combustion; and

igniting said intermediate material and combusting same to produce said metal oxide powder.

2. The process of claim 1, wherein said amino acid compound comprises glycine.

3. The process of claim 1, wherein the anion of said metal salt comprises a nitrate compound.

4. The process of claim 1, wherein said combustion step is conducted at a temperature which will consume substantially all of said amino acid compound, but will neither substantially melt said metal oxide powder nor cause the loss of said volatile metal oxide components causing a substantial loss of stoichiometry or the formation of incorrect crystalline phases.

5. The process of claim 1, wherein the cation of said metal salt comprises any one of aluminum, calcium, chromium, manganese, iron, nickel, copper, strontium, yttrium, zirconium, silver, barium, lanthanum, bismuth, lithium, sodium, magnesium, potassium, scandium, zinc, rubidium, cadmium, indium, cesium, mercury, thallium, lead, cerium, praseodymium, nedymium, samarium, europium, gadolianium, terbium, dysprosium, holmium, cobalt, zinc, hafnium, molybdenum, erbium, thulium, ytterbium, lutetium, uranium and thorium, respectively.

6. The process of claim 1, wherein said metal oxide powder comprises any one of lanthanum strontium chromite, yttrium calcium chromite, lanthanum strontium manganite, yttrium calcium manganite, ceria-zirconia, alumina-zirconia, lanthanum strontium aluminum chromite, yttrium barium copper oxide, bismuth calcium strontium copper oxide, nickel oxide-nickel ferrite, yttria-stabilized zirconia, calcium zirconate, strontium zirconate, manganese ferrite, and lanthanum strontium ferrite.

7. The process of claim 1, wherein said metal salt comprises any one of lanthanum nitrate hydrate, strontium nitrate, chromium nitrate hydrate, yttrium nitrate hydrate, calcium nitrate hydrate, barium nitrate, copper nitrate hydrate, bismuth nitrate hydrate, strontium nitrate, nickel nitrate hydrate, iron nitrate hydrate, zirconium nitrate pentahydrate, yttrium nitrate hexahydrate, manganese nitrate tetrahydrate, iron nitrate hexahydrate, and lanthanum nitrate hexahydrate, aluminum nitrate nonahydrate, cerium nitrate hexahydrate, cobalt nitrate hydrate, zinc nitrate hydrate, hafnium nitrate hydrate, and molybdenum nitrate hydrate.

8. The process of claim 1, wherein the anion of said metal salt comprises any one of an acetate, formate, halide, oxyhalide, sulphate, carbonate and nitrate compound.

9. The process of claim 1, wherein the primary particle diameter of the metal oxide powder is in the range of about 10 to 700 nm.

10. The process of claim 1, wherein said amino acid compound comprises any one of glycine, alanine, valine, leucine, isoleucine, proline, aspartic acid, glutamic acid, lysine, arginine, histidine, asparagine, glutamine, serine, threonine, phenylalanine, tyrosine, and tryptophan.

11. The process of claim 1, wherein the primary particle diameter of the metal oxide powder is in the range of about 100 to 300 nm.

12. The process of forming a substantially homogeneous, precursor aqueous mixture for use in producing metal oxide powders, which comprises

providing at least one substantially soluble metal salt; and

combining said metal salt with a substantially soluble, combustible amino acid to form said precursor mixture.

13. The process of claim 12, which further includes the step of evaporating said precursor aqueous mixture to form an evaporated intermediate material.

14. The process of claim 12, wherein said evaporated intermediate material comprises a viscous liquid intermediate.

15. The process of claim 12, which further includes the step of igniting said intermediate material to form a metal oxide powder.

16. The process of claim 12, which further includes the step of volatizing said metal oxide powder to drive off substantially all of the remaining carbon and metal salt anion, respectively.

17. The process of claim 12, wherein said metal oxide powder has a particle size of not more than one micrometer.

18. The process of claim 12, wherein said metal oxide powder comprises a single crystalline phase.

19. The process of claim 12, wherein the primary particle diameter of the metal oxide powder is in the range of about 10 to 700 nm.

20. A substantially homogeneous, precursor mixture for use in producing metal oxide powders, which comprises

at least one substantially soluble metal salt; and

a substantially soluble, combustible amino acid, which combined with said metal salt forms said precursor mixture.

21. The mixture of claim 20, wherein said amino acid compound comprises glycine.

22. The mixture of claim 20 wherein the anion of said metal salt comprises a nitrate.

23. The mixture of claim 20, wherein the cation of said metal salt comprises any one of aluminum, calcium, chromium, manganese, iron, nickel, copper, strontium, yttrium, zirconium, silver, barium, lanthanum, cerium, cobalt, zinc, hafnium, molybdenum and bismuth, lithium, sodium, magnesium, potassium, scandium, zinc, rubidium, cadmium, indium, cesium, mercury, thallium, lead, cerium, praseodymium, nedymium, samarium, europium, gadolianium, terbium, dysprosium, holmium, cobalt, zinc, hafnium, molybdenum, erbium, thulium, ytterbium, lutetium, uranium and thorium, respectively.

24. The mixture of claim 20, wherein the anion of said metal salt comprises any one of acetates, formates, halides, oxyhalides, sulphates, carbonates and nitrates.

25. The mixture of claim 20, wherein said amino acid compound comprises any one of glycine, alanine, valine, leucine, isoleucine, proline, aspartic acid, glutamic acid, lysine, arginine, histidine, asparagine, glutamine, serine, threonine, phenylalanine, tyrosine, and tryptophan.

26. A process for producing a metal oxide powder which comprises

forming a substantially homogeneous, aqueous precursor mixture comprising at least one substantially soluble metal compound and a substantially soluble, combustible co-reactant compound;

evaporating said precursor mixture to a total solids level which will support combustion; and

igniting said evaporated precursor mixture and combusting same to produce said single phase metal oxide powders.

27. A method of forming oxide ceramic films, which comprises use of an aqueous solution of soluble metal salts and a low molecular weight amino acid, coating said solution onto a substrate, and pyrolyzing said film.

28. A method as defined in claim 27, wherein said metal salt is a nitrate.

29. A method as defined in claim 27, wherein said low molecular weight amino acid is glycine.

30. A method as defined in claim 27, wherein said ceramic film is zirconia, ZrO_2.

31. A method as defined in claim 27, wherein said ceramic film is zirconia stabilized with yttria, $(Zr, Y)O_2$.

32. A method as defined in claim 27, wherein said film is $YBa_2Cu_3O_{7-x}$.

33. A method as defined in claim 27, wherein said film is lanthanum strontium chromite, $(La, Sr)CrO_3$.

34. A process for producing a metal oxide powder or a metal oxide thin film, which comprises

forming a substantially homogeneous, aqueous precursor mixture comprising at least one substantially soluble metal salt and a substantially soluble amino acid compound; and

forming either one of a metal oxide powder and a metal oxide thin film;

the process for forming said metal oxide powder comprising evaporating said precursor mixture to produce a substantially homogeneous intermediate material having a total solids level which will support

combustion; and igniting said intermediate material and combusting same to produce said metal oxide powder; and

the process for forming said metal oxide film comprising coating said mixture onto a substrate, and pyrolyzing said coated substrate to produce said film.

35. The process of claim 1, wherein ammonium mitrate and additional combustible co-reactant compound are added to increase the ash bulk volume.

36. The process of claim 12, wherein said metal oxide powder comprises mixed crystalline phases.

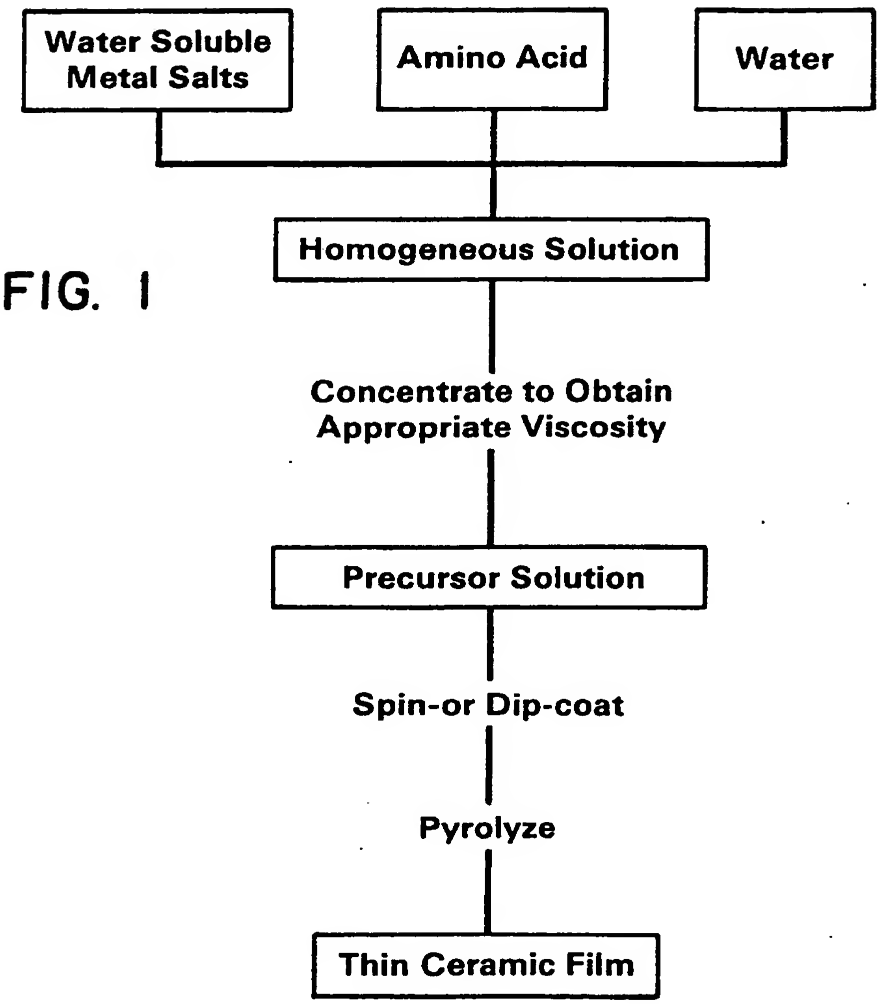

Water Soluble Metal Salts
Amino Acid
Water
Homogeneous Solution
Concentrate to Obtain Appropriate Viscosity
Precursor Solution
Spin-or Dip-coat
Pyrolyze
Thin Ceramic Film

FIG. 1

FIG. 2

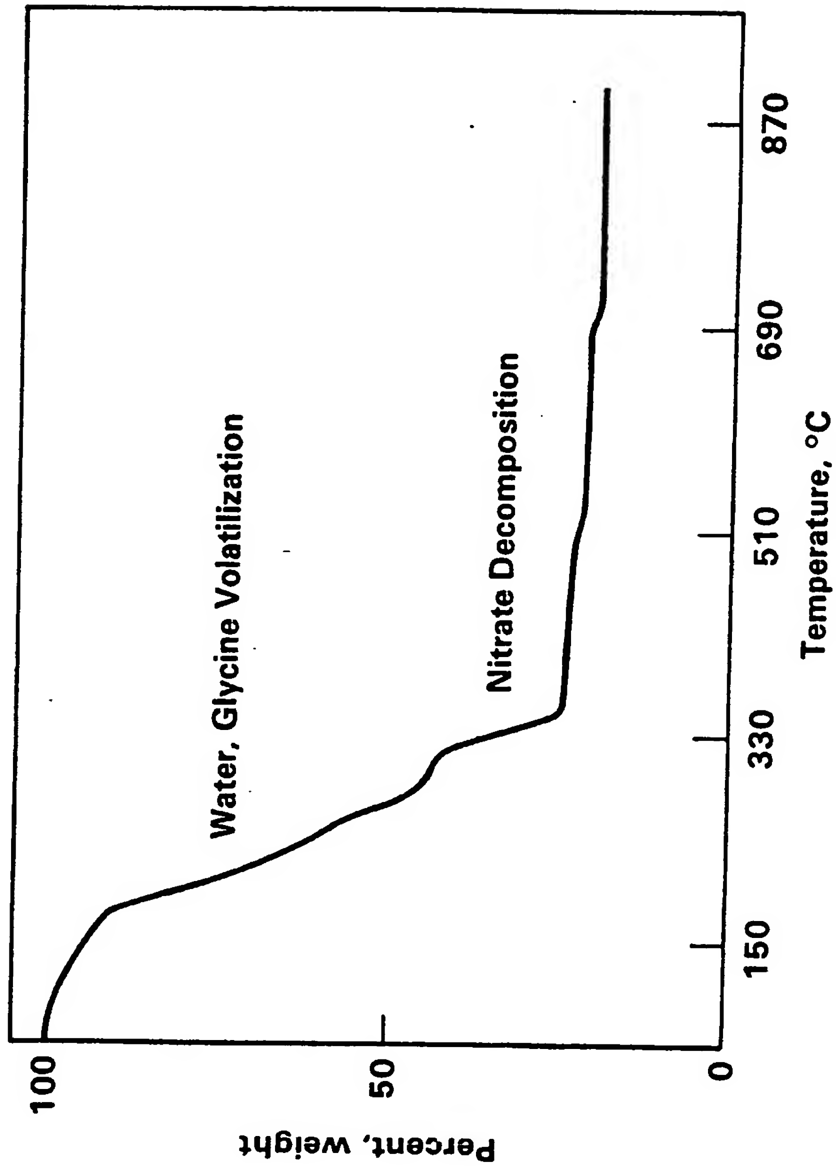

Water, Glycine Volatilization
Nitrate Decomposition
Percent, weight
100
50
0
150
330
510
690
870
Temperature, °C

FIG. 3

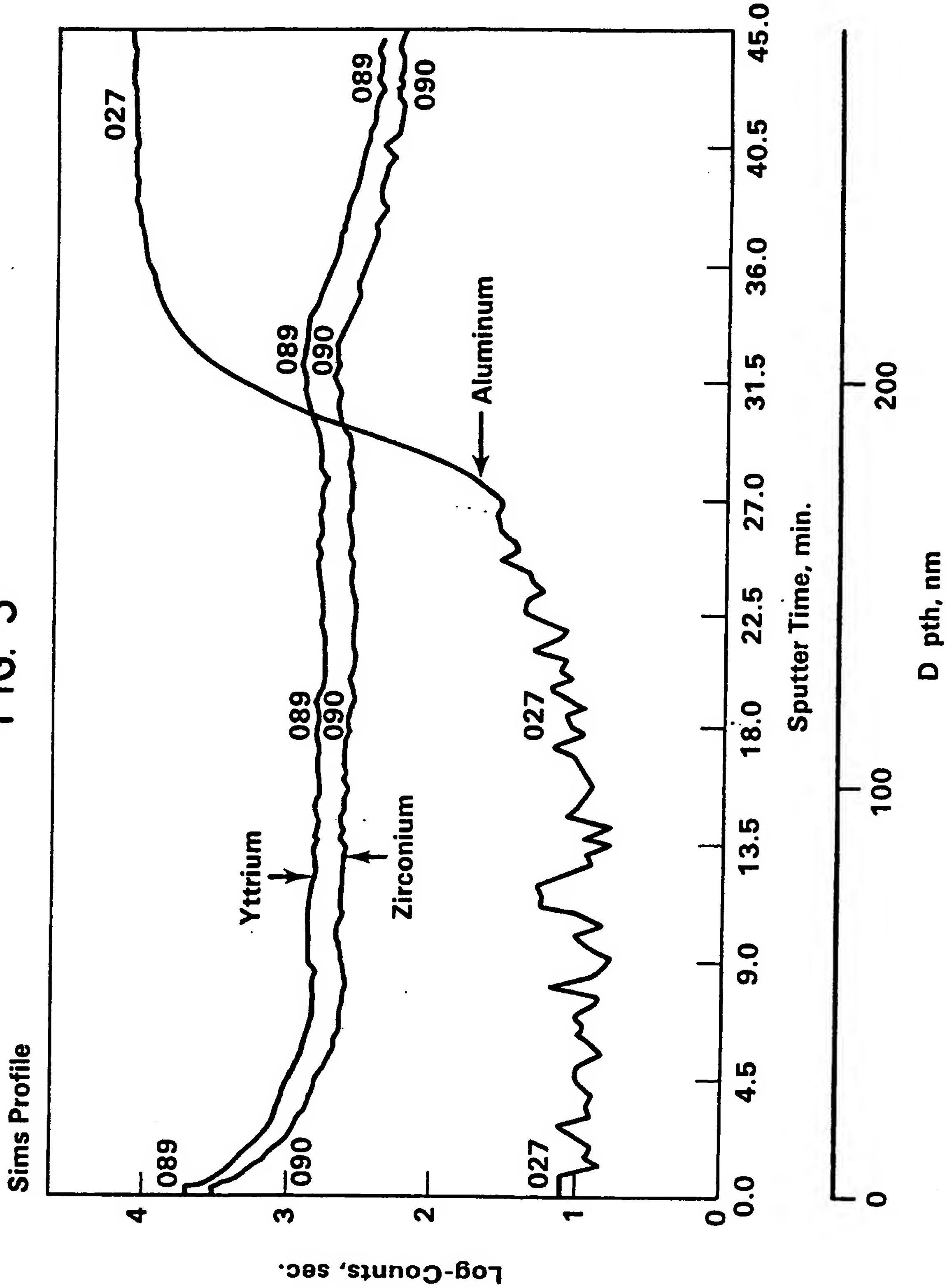
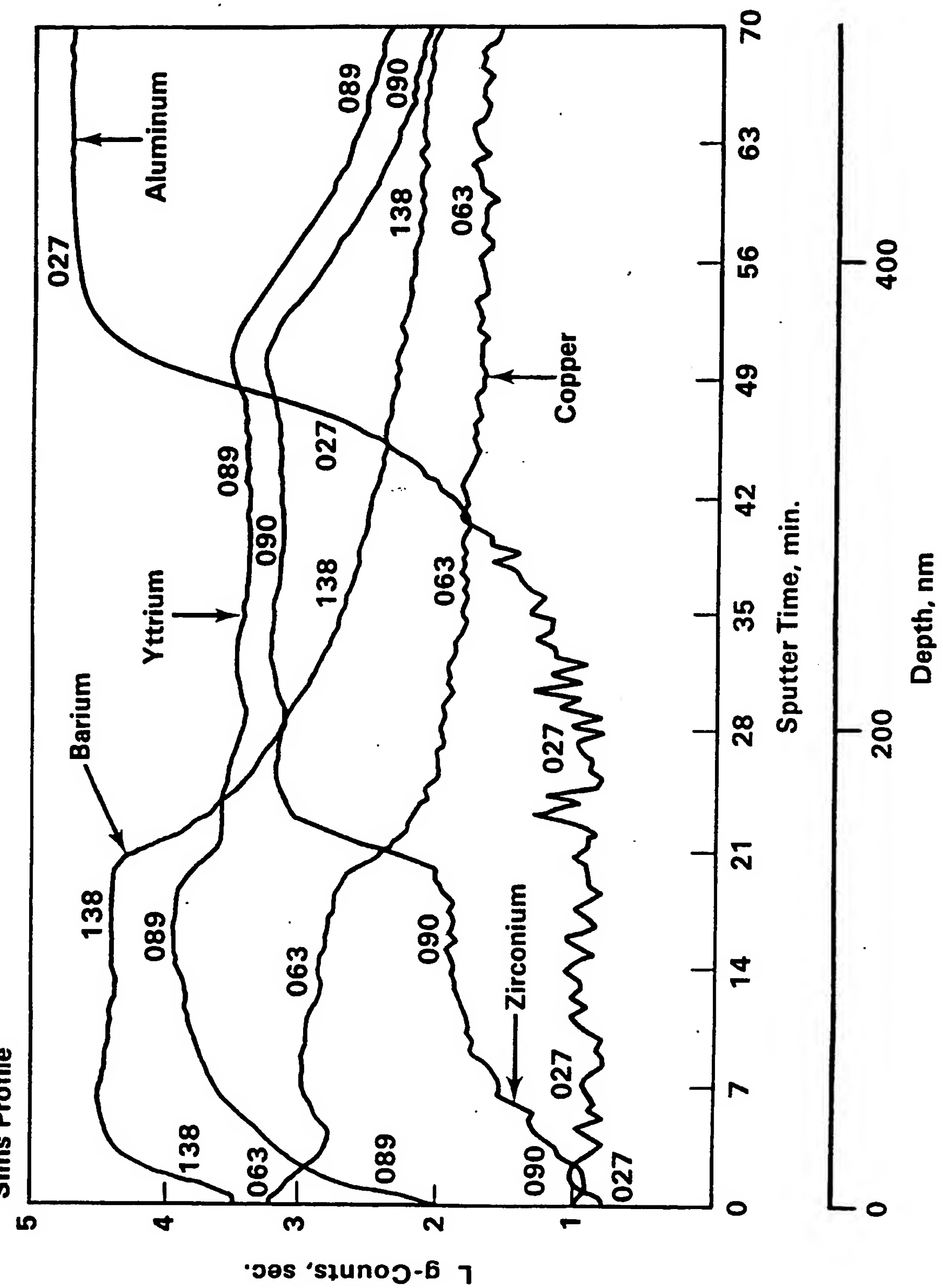

Sims Profile
089
090
027
Yttrium
Zirconium
Aluminum
Log-Counts, sec.
0
1
2
3
4
0.0
4.5
9.0
13.5
18.0
22.5
27.0
31.5
36.0
40.5
45.0
Sputter Time, min.
0
100
200
D pth, nm

FIG. 4


Sims Profile
Barium
Yttrium
Aluminum
Zirconium
Copper
138
089
090
063
027
Sputter Time, min.
0
7
14
21
28
35
42
49
56
63
70
Depth, nm
0
200
400
L g-Counts, sec.
1
2
3
4
5

INTERNATIONAL SEARCH REPORT

International Application No PCT/US89/02528

I. CLASSIFICATION OF SUBJECT MATTER

INT. CL.(4) C01F 17/00; C01B 13/14; C01G 3/02; C01G 49/00; ***
U.S. CL. 423/263, 266, 604, 594; 501/135; 505/1

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System	Classification Symbols
U.S.	423/263, 265, 266, 593-596, 604, 605, 606, 607, 608, 625, 632, 636, 639; 505/1; 501/123,135,152,153;427/62 63,226,168;252/521, 502/355

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 2,763,569, (Bradstreet et al.), 18 September 1956, See claims	1-36
Y	US, A, 3,872,027, (Christmann et al.), 18 March 1975, See examples and claims	1-36
Y	US, A, 3,893,821, (Davies et al.), 08 July 1975, See abstract and claims	1-36
Y	US, A, 4,029,738, (Courty et al.), 14 June 1977, See column 3	1-36
Y	US, A, 4,038,336, (Besozzi et al.), 26 July 1977, See column 3	1-36
Y	US, A, 4,077,808, (Church et al.), 07 March 1978, See column 6	1-36
Y	US, A, 4,293,534, (Arendt), 06 October 1981, See column 3 and claims	1-36
Y	US, A, 4,295,868, (Hölter et al.), 20 October 1981, See column 2	1-36
Y	US, A, 4,473,452, (David), 25 September 1984, See column 3 and claims	1-36
Y	US, A, 4,508,841, (Onuma et al.), 02 April 1985, See columns 2 and 3	1-36

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
15 August 1989	11 OCT 1989
International Searching Authority	**Signature of Authorized Officer**
ISA/US	Paige C Harvey Paige C Harvey

Form PCT/ISA/210 (second sheet) (Rev.11-87)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 4,589,969, (Yurkov et al.), 20 May 1986, See column 2	1-36
Y	US, A, 4,742,030, (Masaki et al.), 03 May 1988, See columns 2 and 3	1-36
A,P	US, A, 4,772,511, (Wood et al.), 20 September 1988, See columns 2-6	1-36
A,P	US, A, 4,772,576, (Kimura et al.), 20 September 1988, See claims	1-36
A,P	US, A, 4,804,649, (Sherif), 14 February 1989, See claims	1-36
Y	Japanese Journal of Applied Physics, vol. 26, No. 10, October 1987, Maki Kawai et al., "Formation of Y-Ba-Cu-O Superconducting Film By Spray Pyrolysis Method" pages L1740-L1742	1-36
Y	Mat. Res. Soc. Symp. Proc, vol. 99, 30 November 1987, Maki Kawai et al., "Properties of Y-Ba-Cu-O Films Formed By Spray Pyrolysis Method" pages 331-334	1-36
X Y	JP, A, 62-59531 (UBE.IND. LTD.), 16 March 1987, See Abstract	1,2,5,10,12-18,20,21,23 25,26,34,36 27-33, 35

International Application No PCT/US89/02528

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

***C04B 35/46; C01F 11/02; B05D 3/02

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE[1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter[12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out[13], specifically:

3. ☐ Claim numbers____________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING[2]

This International Searching Authority found multiple inventions in this international application as follows:

See attached form, telephone practice

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Extra Sheet 1

CONTINUATION OF VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

I. Claims 27-34 drawn to a process of making an oxide ceramic film.

Claim 6 was broken down into 7 species.

II. Claims 1-26 and 34-36 drawn to a process of making an oxide powder alumina-zirconia.

III. Claims 1-26 and 34-36 drawn to a process of making oxide powder, lanthanum strontium chromite, yttrium calcium chromite, lanthanum aluminum strontium chromite, yttrium calcium manganite, lanthanum strontium manganite, lanthanum strontium ferrite and ceria-zircona.

IV. Claims 1-26 and 34-36 drawn to a process of making oxide powder, yttrium barium copper oxide.

V. Claims 1-26 and 34-36 drawn to a process of making oxide powder, bismuth calcium strontium copper oxide.

VI. Claims 1-26 and 34-36 drawn to a process of making oxide powder, manganese ferrite, nickel oxide - nickel ferrite.

VII. Claims 1-26 and 34-36 drawn to a process of making oxide powder, zirconia-stabilized yttria.

VIII. Claims 1-26 and 34-36 drawn to a process of making oxide powder, calcium zirconate, strontium zirconate.